UNITED STATES DISTRICT COURT
DISTRICT OF DELAWARE

- -X

SIEMENS MEDICAL SOLUTIONS USA,
INC.,

Civil Action No. 07-190 (SLR)

Plaintiff,

v.

**REDACTED
PUBLIC VERSION**

SAINT-GOBAIN CERAMICS & PLASTICS,
INC.,

Defendant.

- -X

DECLARATION OF DR. KENNETH J. McCLELLAN

Kenneth J. McClellan, of full age, declares as follows:

Background and Credentials

1.   I am a research scientist at the Los Alamos National Laboratory working in the

field of Materials Science and Engineering with experience in development of rare earth

oxyorthosilicate scintillators. I have been involved in materials science and engineering

with an emphasis on ceramic materials for over twenty years where materials science is

the term used for the broad field that encompasses material synthesis and material

behavior across the range of material types, i.e. metals, intermetallics, ceramics, glasses

and polymers. The field of materials science incorporates substantial components of

solid state chemistry, solid state physics, mechanical engineering, electrical engineering

and metallurgy. The majority of my career has been spent in the study and development

of new materials for technical applications. A significant component of my novel

material preparation has been in the area of scintillator materials for applications

involving radiation detection.

Education and Experience

2.   I received my B.S., M.S. and Ph.D. degrees in the areas of Materials Science and

Engineering from Case Western Reserve University, writing my dissertation on the role

of defects on the structure/property relationships of solid solution alloys in the yttrium

oxide-zirconium oxide system. The title of my dissertation was "Structure/Property

Relations in Y_2O_3-Stabilized Cubic ZrO_2 Single Crystals" and this was the first of a

number of research activities where I have studied alloys in which yttrium was a key

component that determined a material's properties.

3.   After receiving my Ph.D. in 1994, I took a postdoctoral appointment in the

Ceramic Science and Technology group at Los Alamos National Laboratory ("LANL")

working on novel material creation and development. I accepted a position as a technical

staff member in that group in 1996 where I established the Single Crystal Growth

Laboratory focusing on high temperature growth of ceramic single crystals from the melt

for programs ranging from basic science to national security applications. Depending

upon the material being studied there are typically several methods available to grow

crystals, and I have specialized in growing crystals from the liquid state after the

compound has been heated above the melting point, i.e. growth from the melt. This is the

type of growth that is used for the Y_2SiO_5 ("YSO"), Lu_2SiO_5 ("LSO"), and $(Lu,Y)_2SiO_5$

("LYSO") scintillator crystals involved in the current case.

4.   In 1997 I transferred my team and operations to the Structure/Property Relations

group at LANL where I subsequently increased my activities in the area of scintillator

development for national security applications (weapons diagnostics, nuclear

nonproliferation, special nuclear material detection, and other related technological

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applications). I have continued my material development activities in this group and currently hold the position of Team Leader for the Thermodynamics and Kinetics of Materials team. This is a team that integrates both experimental and computational staff for material development via understanding and control of defects in materials. (A copy of my current curriculum vitae is annexed hereto as Exhibit A).

Expertise in Rare Earth Oxyorthosilicate Scintillators

5.   In connection with my work at LANL, I have been intimately involved in the development of an LYSO crystal. It is based upon my expertise relevant to development of cerium-activated LYSO (LYSO:Ce or LYSO throughout) and related scintillator materials that I was retained as an expert witness in this case by Thelen Reid Brown Raysman & Steiner LLP on behalf of defendant Saint-Gobain Ceramics & Plastics, Inc. I am being compensated at a rate of $175/hr for my services in this action, and while I am currently employed at LANL, the opinions expressed in this declaration are solely mine and are not to be attributed to LANL (operated by Los Alamos National Security) or the US Department of Energy ("DOE").

6.   Of particular relevance to the current case is my past involvement as work package manager for scintillator development on the DARHT (Dual-Axis Radiographic Hydrodynamic Test) facility construction project at LANL. This is a one-of-a-kind facility designed to take multiple x-ray images through solid objects as the object is deformed under explosive conditions. It was in this role that I investigated new cerium-activated scintillator materials in the Y_2SiO_5- Lu_2SiO_5, Y_2SiO_5- Gd_2SiO_5, and Gd_2SiO_5-Lu_2SiO_5 systems for application in the solid state imaging system. Based upon our experimental results of growth characteristics and scintillator performance weighed against the various overall x-ray imaging system design specifications, I eventually chose

to develop a cerium activated Y_2SiO_5- Lu_2SiO_5 solid solution alloy with a 1:9 ratio of the end member compositions. This directly equates to the $Lu_{1.8}Y_{0.2}SiO_5$:Ce composition that is of interest to the present case as it is the basic composition of the Saint-Gobain LYSO scintillator crystal designated as PreLude 420.

7.   I chose this composition based upon a combination of criteria designed to obtain four sequential x-ray images in two microseconds from a high energy pulsed x-ray source during an explosive event. Primary scintillator design specifications included a high level of prompt light output, short decay time, relatively high density (>7 g/cm^3), emission wavelength appropriate for a lens-coupled, charge-couple device (CCD) image acquisition system, low optical absorption for the scintillation emission, low afterglow, and relatively low self-excitation, i.e. low background. ^{176}Lu is a naturally occurring radioactive isotope of lutetium with an abundance of ~2.59% which effectively generates a background noise in the detected signal [1][1]. There is substantial overlap between the scintillator performance characteristics for the DARHT application and for use in a Positron Emission Tomography ("PET") scanner. These characteristics include emission wavelength compatible with the rest of the imaging system, high effective atomic number to provide a high probability of the x-ray or gamma ray interacting with the scintillator crystal, high quantum efficiency so that a large amount of light is generated from an interaction and that light is able to escape the crystal into the rest of the imaging system, fast decay of the scintillation light for timing, and low afterglow so that the emission signal is not lost in the background signal.

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[1] Bracketed numerals in the body of the text of this declaration denote end-note references, which are set forth in the document annexed hereto as Exhibit B.

8.   In addition to the optical performance characteristics, suitability to efficient

growth of high quality single crystals from the melt was also a major factor in selecting

the scintillator composition for development. Suitability for efficient growth means that

the crystals can be grown in large sizes ($\geq$ 5 centimeters (cm) in diameter, with total

lengths on the order of 30 cm or longer), with a high yield of material possessing the

required performance characteristics (the scintillation properties vary along the length of

a given crystal so typically only a fraction of a grown crystal is usable), and that this can

be achieved in an economical operation (rare earth oxyorthosilicate crystal growth is

relatively expensive due to the cost of 1) high purity, raw powders, 2) precious metal

components to contain the molten compound, 3) high temperature insulation materials

required for these crystals with melting points of $\geq$2000 °C, 4) the energy required to

perform crystal growth at temperatures $\geq$2000 °C, and 5) the large waste associated with

crystals that are damaged or that do not meet performance specifications). Therefore both

performance and manufacturing issues are important for scintillator crystals for the PET

market or any commercial application requiring large quantities of scintillator crystal

(tens of kilograms of crystal per unit).

9.   My team did substantial development of the $Lu_{1.8}Y_{0.2}SiO_5:Ce$ scintillator crystal,

and I was granted a patent (U.S. Patent No. 6,323,489 (the "'489 patent"), a copy of

which is annexed hereto as Exhibit C) that was originally assigned to the Regents of the

University of California for scintillator crystals with the composition of $Lu_{(2-x-z)}Y_xCe_zSiO_5$ where $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$ and the use of those crystals in a

detector[2]. Some aspects of the development of this crystal were presented in open

meetings and originally published in 2000 [3]. An interference was declared against the

'489 patent based upon a provisional patent filed by B. Chai and Y. Ji. Due to technical

reasons associated with patent law, the '489 patent was ultimately surrendered and U.S.

Patent No. 6,624,420 (the "'420 patent") was issued covering the relevant compositions.

It is my understanding that the $Lu_{1.8}Y_{0.2}SiO_5$:Ce scintillator crystal has been licensed to

Saint-Gobain under the '420 patent.

Basis for Opinion

10.   In preparing this declaration, I have reviewed the complete set of papers

submitted in support of Siemens Medical's[2] pending motion with particular attention to

the US 4,958,080 patent, the affidavit of Niraj Doshi, and the affidavit of Marvin J.

Weber in regard to the claims made by the Plaintiff. I also reviewed related patents and

technical articles. A complete list of the documents I considered is annexed to this

declaration as described below. My opinions are based upon these documents, my

experience with the scintillator crystals under consideration, and my expertise as a

materials scientist in the area of scintillator development.

Opinion

11.   Based upon my extensive experience with this crystal, the creation of LYSO is

not an insubstantial change over the LSO crystal and based upon the patents granted

('489 then '420) the patent office agrees. LYSO possesses substantial advantages over

LSO in terms of performance and manufacture.

12.   I have reviewed the documents filed in support of Siemens Medical's pending

motion and find the assertions (paraphrased here by the author) that 1) LYSO is not a

unique scintillator crystal, 2) that LYSO is equivalent to LSO with a "dash" of yttrium

which has no effect on scintillator characteristics, and 3) that the LYSO crystal was

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[2] "Siemens Medical" denotes references to plaintiff Siemens Medical Solutions USA, Inc.

developed only as a way around the '080 patent for the PET market to be incorrect and contrary to the existing data. In regard to the affidavit of Marvin J. Weber, while agreeing with the statements regarding fundamental mechanisms governing scintillation in activated, inorganic scintillator crystals, it is my opinion that his affidavit is so limited in its analysis of the characteristics of the scintillator crystal in question (he specifically notes that his analysis is restricted to the comparison of LSO and LYSO in the context of the '080 patent) that it does not properly represent the unique nature of the $Lu_{1.8}Y_{0.2}SiO_5$:Ce (LYSO) scintillator crystal, especially with regard to the unique advantages of LYSO in terms of: 1) the ability to tailor performance characteristics relative to the "pure" end member oxyorthosilicates, i.e. YSO and LSO, 2) the ability to improve manufacture of the scintillator crystal relative to the end members, and 3) the critical role of crystalline lattice defects (imperfections in atomic type and position relative to an "ideal" arrangement of atoms within the crystal structure) on scintillator performance. The ability to tailor scintillator performance and to balance that performance against fabrication considerations is one of the reasons that the LYSO composition is considered as a unique scintillator material.

Approach for Discussing Compositions

12.   When considering combining elements to make new materials, the combinations are effectively infinite. Therefore, it is often convenient to view compositions in terms of "end members," and these end members can be the individual atomic constituents or compounds themselves. For instance, at the most basic level, under normal pressures, the end members of the binary compositional systems Y-O, and Si-O can be combined in the ratios of 2:3 and 1:2, respectively, to form Y_2O_3 and SiO_2. Various combinations of Y_2O_3

Fig 1a)

Y_2SiO_5

Y_2O_3 1:1 SiO_2

Fig 1b)
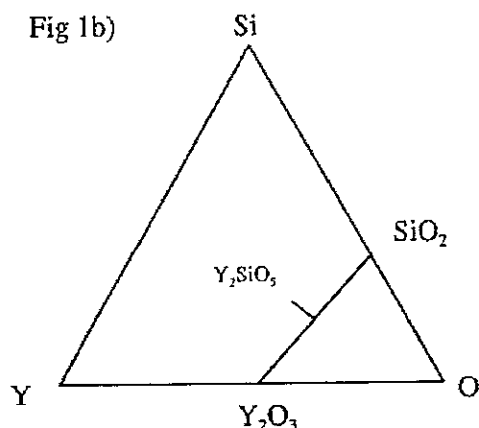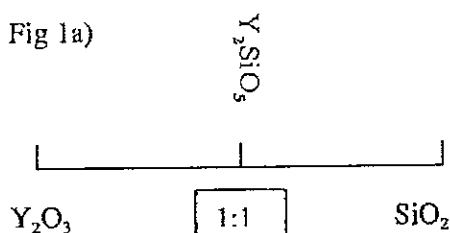
and SiO_2 can then be formed with new compounds being formed at specific compositions, e.g. a 1:1 ratio will form Y_2SiO_5 (YSO). This can be considered as a pseudo-binary system where the compositions effectively fall on a line between the end members (Fig 1a). A more complex representation of the combinations of these elements would be the Y-Si-O system where compositions fall within a triangle bounded by the end members, Y, Si, and O (Fig 1b). The three compounds indicated are relevant to the current discussion but are in no way the only ones that exist in this three element system. The area contained within the triangle in figure 1b illustrates the continuum of compositional possibilities in even this simple system. A similar representation could be made for the Lu-Si-O system that contains LSO. Within a given compositional space, materials can form new compounds with atomic arrangements different from the end members, such as the Y_2O_3, SiO_2, and Y_2SiO_5 compounds indicated, or they can form mixtures of the end members which herein are referred to as solid solutions or alloys. As the number of components in a chemical system increases the compositional possibilities increase accordingly. The compositions that correspond to discrete structures and those that correspond to mixtures are not known

a priori and the individual properties of any given composition are not known until it is made and tested.

LYSO Is Recognized as a Unique Scintillator Material

14.   For the following discussion, the Y-Lu-Ce-Si-O system is simplified as a pseudo-binary system of Y_2SiO_5:Ce and Lu_2SiO_5:Ce, i.e. YSO-LSO. By "pseudo-binary" I mean the description of a crystal as if it contained only two variables, whereas LSO and YSO in fact contain many variables (including yttrium and lutetium, silicon, oxygen and so forth). In the range of compositions between YSO and LSO there are no known phases with a different crystal structure so each composition will have its own characteristics, some of which will be similar to an end member, some of which may be some combination of the end member characteristics and some of which may be completely different. For solid solutions no characteristic is likely to be exactly the same as that for an end member. The view that the solid solutions in the rare earth oxyorthosilicate crystals are unique crystal compositions is supported broadly in the field of materials science but particularly by the technical articles discussing the relative merits of the crystals in the various LSO-GSO-YSO pseudo-binary systems (i.e. LSO-GSO, LSY-YSO, and GSO-YSO, *cf.* [4-7]) as well as several existing US patents which claim unique end member and solid solution compositions in the family of rare earth oxyorthosilicate compounds (*cf.* [8-11]).

15.   With respect to the current claims by Siemens Medical Solutions USA, Inc that LYSO is equivalent to LSO, one of the most telling examples supporting the existence of LYSO as a unique scintillator composition is the paper entitled "Investigation of the properties of new scintillator LYSO and recent LSO scintillators for phoswich PET detectors" which is co-authored by Charles L. Melcher, the inventor of the '080 patent,

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and specifically describes an LYSO solid solution composition as a new scintillator[7]. The authors state: "A variant of LSO in which some of the lutetium is replaced by yttrium atoms has recently been developed at CTI, Inc. (Knoxville, TN)[3]. Cerium-doped lutetium-yttrium oxyorthosilicate ($Lu_{0.6}Y_{1.4}SiO_5$:Ce, LYSO) has comparable light yield to LSO with a slightly longer decay time of 53 ns (authors note: ns is nanosecond or 1/1,000,000,000th of a second), making it an attractive candidate for PSD[4] identification in phoswich detectors. In this work, the scintillation performance of the **new LYSO scintillator** (emphasis added) was investigated…and compared to the most recent LSO production." Another example arguing for the unique existence of solid solution scintillator compounds is US patent 5,264,154 which claims cerium-activated scintillator crystals represented by the formula $Gd_{2-(x+y)}Ln_xCe_ySiO_5$ where Ln is at least on element of Sc, Tb, Dy, Ho, Er, Tm, Yb, and Lu with contents ranging from $0.1 \leq x \leq 0.7$, i.e. LGSO is claimed where the gadolinium in the end member composition GSO is replace by 10 atomic percent or more of lutetium[12]. Again here C. L. Melcher is a co-inventor of this range of new scintillator crystals composed of LGSO.

LYSO and LSO Have Similarities and Differences

16.   The view that the LYSO scintillator is indeed a new scintillator is consistent with the established understanding in the field of materials science that the compositions intermediate between two chosen compositional end points will exhibit some properties that are similar to an end member and some properties that are different from the end members. The similarities and differences are generally not known *a priori*, and while knowledge of a relevant physical phenomena (such as melting behavior, thermal

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[3] I understand that CTI Inc. is a predecessor of Siemens Medical.
[4] PSD is defined as "pulse shape discrimination" in that reference

conductivity, mechanical strength, scintillation efficiency, etc) in a given alloy is often

estimated based on "rules-of-thumb," specific properties rarely can be accurately

predicted and must be experimentally determined. It is true that many properties change

gradually, but based on my experience in materials science, the statement that 10 mole

percent of yttrium with respect to the rare earth elements in the oxyorthosilicate structure

($Lu_{1.8}Y_{0.2}SiO_5$:Ce (90/10 LYSO)) substitutes "a small amount of lutetium in the LSO

crystals claimed in the'080 patent with a **dash** (emphasis added) of another rare earth

element (yttrium) that has similar properties" as stated in the Plaintiff's opening brief is

not a correct statement.

17.   In the field of scintillator crystals, substantial performance differences are often

associated with activator or impurity contents at the levels of several parts per million

(ppm). This is especially true of the rare earth elements (including Ce, Lu and Y) as they

are associated with a large fraction of the optical materials developed for technical

applications, e.g. lasers and scintillators. Indeed, the cerium activator that enables the

scintillator crystals of interest here is included at the ppm levels. On the other hand, the

yttrium content in the PreLude 420 scintillator is ~10 at% which equates to ~100,000

ppm, a level three to four orders of magnitude higher than the enabling Ce activator in the

same crystal.

18.   As indicated above, the characteristics of a given composition can be estimated

based upon experience and intuition but cannot be definitively predicted. For instance,

due to the cost and difficulty in getting raw, highly pure lutetium oxide powders for

crystal growth, industry and researchers have continuously sought to find other rare earth

compositions for a given application. In the area of rare earth oxyorthosilicates, two

promising candidates La_2SiO_5:Ce and Yb_2SiO_5:Ce were considered. La_2SiO_5:Ce crystals were not even able to be grown using standard techniques[13]. Attempts to use the related rare earth lattice element ytterbium, which is similar to Lu in many characteristics (it is adjacent in the periodic table), showed successful growth of the single crystals but the Yb suppressed the Ce emission in the oxyorthosilicates, via a parasitic charge transfer which quenches the light output[14], i.e. the crystal was transparent and dense but not bright.

19.   Accordingly, while yttrium was readily anticipated to be a viable lattice constituent based on the success of YSO scintillators, the success of the LYSO scintillator was not known until the crystal had been made and tested. The mixture of Y^{3+} and Lu^{3+} ions in the LYSO distorts the structure relative to either of the end member compositions, LSO and YSO. Specifically, the yttrium in LYSO can be considered to "open up" the crystalline lattice relative to LSO due to its large atomic size[15] (author's note: The Weber affidavit switches the radii for Y^{3+} and Lu^{3+} at the top of page 11, therefore incorrectly stating that the lutetium ion is larger than the yttrium ion when according to the referenced work of R. D. Shannon – which is broadly accepted as the authoritative reference for these values- the reverse is true). This distortion changes the lattice and provides both advantages and disadvantages to scintillator performance and manufacture relative to LSO.

Performance Effects of Mixed Y and Lu

20.   The process of scintillation in activated, inorganic crystals can be broken into three primary stages, namely: 1) interaction of the incident radiation with the scintillator crystalline lattice and subsequent creation of electron-hole pairs, 2) translation of the energy to a luminescent center (activator ion) via transport of the electrons and holes

through the lattice, and 3) relaxation of an activator ion from a resulting excited state by emission of light. This process while presented as three stages rather than four is in agreement with the fundamental description of scintillation as described in Weber's affidavit. However, the current description more readily enables a discussion of the role of defects in the scintillator crystal.

21.   The effect of defects in a given class of scintillator crystals is not sufficiently understood as to be able to be predictive in terms of scintillator performance, especially in such complex crystalline structures as the rare earth oxyorthosilicates. Again as stated earlier, individual single crystal compositions must always be grown and characterized to establish such key scintillator characteristics as total light output, the fraction of light which occurs as prompt emission, the decay time, and the existence and magnitude of afterglow. The distortion of the crystalline lattice and existence of point defects in the lattice, such as vacancies, interstitials, and anti-sites, relative to its ideal configuration is what is generally meant in this declaration as "defects" or "point defects."

22.   It is well known that point defects either in the form of intrinsic defects (naturally occurring for synthesis and operation above zero degrees Kelvin) or those associated with activators, dopants and impurities, are at least partially responsible for nonradiative transitions (cf. [16]). A relationship describing the overall scintillator efficiency has been derived by Lempicki et al.[17], based upon a previous description established for phosphors:

$$\eta = \beta S Q, \qquad (1)$$

where β is the conversion efficiency of an incident photon to form electron-hole pairs, S is the transfer efficiency of the electron-hole pairs to the luminescent center, and Q is the

efficiency of luminescence from the center[18]. It is this three stage description of scintillation which was described above, analogous to Weber's description[19]. It follows that values for S (transfer efficiency) are lowered by the presence of defects[20], since they can trap electrons and holes thereby interrupting the energy transfer process. Furthermore, it has been suggested that S represents the most important step in the scintillation process (in terms of overall scintillator efficiency)[21], as it can compensate for poor conversion and luminescence properties. Since S is directly linked to the crystal defects, development and optimization of scintillators is critically dependant upon the defect structure of a crystalline scintillator.

23.   It has been claimed by Siemens Medical that yttrium was knowingly added to LSO by Saint-Gobain as an atomic substitution that would not substantially affect the character of the scintillator relative to that of LSO in order to enter the PET market by infringing on the '080 patent. This is contrary to the prior development of LYSO for national security applications and the broad acceptance of LYSO as a unique scintillator. In addition, while it is true that some important properties of importance for PET scanners are very similar in LSO and LYSO (as well as YSO), it is incorrect to represent that the LYSO solid solution of the LSO and YSO end member compositions is functionally equivalent to LSO. The incorporation of yttrium atoms into the oxyorthosilicate structure at the 10 atomic percent (PreLude 420) level will perturb the lattice relative to the end member compositions enabling tailoring of specific properties such as background optical emission due to naturally occurring radioactive isotope, prompt emission light output, afterglow, and density. Indeed the advantages of YSO and

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LYSO relative to LSO in terms of detrimental afterglow is the subject of a recent patent for performance improvements in LYSO[22].

24.   By way of example, the effects of yttrium incorporation in terms of rare earth cation distribution in the C2/c oxyorthosilicate structure (the general structural arrangement of atoms shared by YSO, LSO, and LYSO), can be examined more closely. Due to the difference in atomic size between Lu, Y and Ce[15], it is expected that LYSO compositions allow site occupancy to be biased to favor a non-random distribution of cations (Lu^{3+}, Y^{3+}, Ce^{3+}, Ce^{4+} on the two none-equivalent rare earth cation sites (RE1 and RE2)). This ability to bias site occupancy and corresponding defects associated with the lattice perturbations in these activated, solid solution compounds can manifest itself in the emission spectrum, decay time, prompt light output and afterglow. The various, interrelated effects associated with site bias have been observed and discussed to some degree in the literature[6, 23, 24]. This author believes that it is these site occupancy bias effects that are clearly seen in the optical emission data presented in Doshi's affidavit. The "shoulders" on the emission curves in his Exhibit G show increased light output relative to the LSO. This shoulder is in the region of emission from the second rare earth site in the oxyorthosilicate structure (RE2) and not only provides additional light output from the crystal but also shifts the average emission to a slightly longer wavelength.

Manufacturing Effects of Mixed Y and Lu

25.   In addition to the ability to tailor specific aspects of optical performance by mixing rare earth cations in the oxyorthosilicate scintillators, yttrium-bearing solid solutions have advantages over LSO in terms of manufacture via reductions in growth

costs per single crystal boule and yield of high quality material per boule. As stated earlier, yttrium "opens up" the lattice relative to LSO which increases the incorporation of Ce (a larger cation) into the boule enabling a increased yield of high quality crystal per growth. The yttrium also suppresses the melting point relative to LSO which provides energy savings as well as savings from decreased attrition of structural components used for crystal growth. Worldwide there is a better infrastructure for manufacture of high purity yttrium oxide powder which translates to lower raw material cost and to reduced issues associated with material impurities. Based upon the combination of the ability to tailor LYSO's optical performance and the advantages in large scale manufacturing it can readily be seen why this unique scintillator is a compelling choice for the PET market.

26.   In summary, it is my considered opinion that LYSO, particularly the composition employed for fabrication of Saint-Gobain's PreLude 420, 1) is indeed a unique scintillator crystal, 2) that it has distinct differences (and advantages) in terms of optical performance and in terms of manufacture, and 3) that it is not simply an equivalent crystal introduced for the purpose of infringing on the '080 patent with regard to application in PET scanners.

27.   I declare under penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

Executed on October 16, 2007

KENNETH J. McCLELLAN

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UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

CERTIFICATE OF SERVICE

I hereby certify that on October 30, 2007, I electronically filed the foregoing document

with the Clerk of the Court using CM/ECF which will send notification of such filing to the

following and which has also been served as noted:

BY ELECTRONIC MAIL AND HAND DELIVERY

Jack B. Blumenfeld
Maryellen Noreika
Morris, Nichols, Arsht & Tunnell LLP
1201 North Market Street
Wilmington, DE 19899

I hereby certify that on October 30, 2007, the foregoing document was sent to the

following non-registered participants in the manner indicted:

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Gregg F. LoCascio
Charanjit Brahma
Sean M. McEldowney
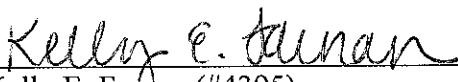Kirkland & Ellis LLP
655 15th Street, N.W.
Washington, DC 20005-5793

Kelly E. Farnan (#4395)

EXHIBIT A

Curriculum Vitae

Kenneth J. McClellan
Structure/Property Relations (MST-8)
MS G755
Los Alamos National Laboratory
Los Alamos, NM 87545

Education

Case Western Reserve University	Metallurgy and Materials Science	B.S./1988
Case Western Reserve University	Materials Science and Engineering	M.S./1991
Case Western Reserve University	Materials Science and Engineering	Ph.D./1994

Appointments

Team Leader , Thermodynamics and Kinetics of Materials	2006-present
Member of Technical Staff, MST-8	1997-2006
Member of Technical Staff, MST-4	1996-1997

Research Activities & Relevant Expertise:

Dr. McClellan established and oversees operation of the Materials Preparation Facility located within the Materials Science and Technology division. His thesis and early research was based on materials for high temperature structural applications with an emphasis on synthesis of single crystal alloys for strengthening mechanism studies. Since becoming a staff member at Los Alamos National Laboratory in 1996, his research has emphasized synthesis of novel or custom-designed materials for many different applications, including ceramic nuclear fuels, scintillators, radiation tolerant and high temperature structural materials. He has experience in preparation of metallic, intermetallic and ceramic materials and in growth of crystals from the melt using a variety of methods with emphasis on intermediate to high temperature growths using floating zone and Czochralski techniques. He has twice been recognized with the Defense Programs Award of Excellence as part of the DARHT project team where the contribution focused on new detector crystal design and preparation, he received a Distinguished Performance Award in 2005 as part of the UN Fuel Fabrication Team, and he holds three patents (with a four submitted) on the preparation and application of novel materials. His contributions as a graduate mentor was also recognized in 2002 with LANL's Distinguished Mentor Award.

Representative Collaborators since 1998

R. Grimes (Imperial College, London); P. Peralta (ASU); J. Garrett (McMaster); J. Gardner (NIST); S. Derenzo (LBNL); A. Sayir (NASA); D. Matthiesen (CWRU); I. Shindo (CSI, Japan); Y. Furukawa (Oxide Corp., Japan); J. Neumeier (MSU); K. Kitamura (NIRIM/NIMS); J. Martinez-Frenandez (Seville); J. Rigney (GE); T.E. Mitchell, J. J. Petrovic, D. W. Cooke, K. Sickafus, E. Bauer (LANL)

Clearance Level

Active DOE "Q" clearance

Publications

1. C. R. Stanek, K. J. McClellan, M. R. Levy, C. Milanese and R. W. Grimes, "The effect of intrinsic defects on $RE_3Al_5O_{12}$ garnet scintillator performance" *Nucl. Instr. Methods B*, **579**[1], pp. 27-30 (2007)

2. C. R. Stanek, K. J. McClellan, B. P. Uberuaga, K. E. Sickafus, M. R. Levy, and R. W. Grimes, "Determining the site preference of trivalent dopants in bixbyite sesquioxides by atomic-scale simulations" *Phys. Rev. B*, **75**, pp. 134101-7 (2007)

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2. Defense Programs Award of Excellence: 2nd axis of DARHT (2002)

3. Los Alamos National Laboratory Distinguished Mentor Award: Graduate Mentor (2002)

4. Defense Programs Award of Excellence: DARHT Project Team (1999)

5. Los Alamos National Laboratory Teamwork Award: DARHT Phase I (1999)

EXHIBIT B

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EXHIBIT C

EXHIBIT C

US006323489B1

(12) **United States Patent**   (10) Patent No.:   **US 6,323,489 B1**
McClellan   (45) Date of Patent: **Nov. 27, 2001**

(54) **SINGLE CRYSTAL SCINTILLATOR**

(75) Inventor: **Kenneth J. McClellan**, Los Alamos, NM (US)

(73) Assignee: **Regents of the University of California**, Los Alamos, NM (US)

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Primary Examiner—Seungsook Ham
Assistant Examiner—Shun Lee
(74) Attorney, Agent, or Firm—Samuel L. Borkowsky

(57)   **ABSTRACT**

The present invention relates to single crystal scintillators and includes a transparent single crystal of cerium-activated lutetium yttrium oxyorthosilicate having the general formula Lu$_{(2-x-z)}$Y$_x$Ce$_z$SiO$_5$, wherein $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$. The crystal scintillator of the present invention is dense, bright, rugged, and non-hygroscopic and has a relatively short decay time for luminescence. The invention also includes a scintillation detector using the crystal scintillator, which produces an electrical signal in response to light received from the crystal scintillator upon exposure to gamma rays, x-rays, and the like.

10 Claims, No Drawings

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SINGLE CRYSTAL SCINTILLATOR

FIELD OF THE INVENTION

The present invention relates generally to single crystal scintillators for detecting radiation and more particularly, to single crystal scintillators having the formula $Lu_{(2-x-y)}Y_xCe_ySiO_5$ where $0.05 \leq x \leq 1.95$ and $0.001 \leq y \leq 0.02$. This invention was made with government support under Contract No. W-7405-ENG-36 awarded by the U.S. Department of Energy to The Regents of the University of California. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Transparent single crystal scintillators are used to detect gamma rays, x-rays, cosmic rays, and other types of radiation, and to detect particles having energies of about 1 KeV and above. When radiation is incident on the scintillator, light pulses are generated by the scintillator that may be optically coupled to the photomultiplier tube of a scintillation detector to produce a voltage signal that is related to the number and amplitude of the light pulses received by the photomultiplier tube. Crystal scintillators are used in digital radiography, medical imaging, mineral and petroleum exploration, and other important applications.

A widely used scintillation detector employs the thallium-doped sodium iodide scintillator, NaI(Tl); it has a very high light output (i.e., is a very bright scintillator) in response to radiation and is relatively inexpensive to produce. Scintillation detectors employing NaI(Tl) are used in logging tools to aid in the location of petroleum deposits.

Inorganic metal oxides are another important group of materials used in scintillation detectors. These include bismuth germanium oxide $Bi_4Ge_3O_{12}$ (BGO) and cerium-activated oxyorthosilicates, which include cerium-activated gadolinium oxyorthosilicate $Gd_{(2-x)}Ce_xSiO_5$ (Ce:GSO), cerium-activated lutetium oxyorthosilicate $Lu_{(2-x)}Ce_xSiO_5$ (Ce:LSO), and cerium-activated yttrium oxyorthosilicate $Y_{(2-x)}Ce_xSiO_5$ (Ce:YSO). The data in The Table below, which is taken from the papers and patents that follow, summarizes relevant physical properties for NaI(Tl), Ce:BGO, Ce:GSO, Ce:LSO, and Ce:YSO. The decay time in nanoseconds refers to the time it takes for a particular scintillator crystal to luminesce from the excited electronic state, which is the time required before the crystal can respond to additional radiation once it been exposed to sufficient radiation to produce an electronically excited state in the crystal. The reported range of decay times for several entries is likely a result of the difficulty in obtaining consistently uniform incorporation of cerium into the product crystal scintillator during crystal growth. The emission peak wavelength in nanometers refers to the wavelength maximum in the emission spectrum for the particular crystal scintillator.

TABLE 1

Property	NaI(Tl)	BGO	Ce:GSO	Ce:LSO	Ce:YSO
Density (g/cm³)	3.67	7.13	6.71	7.4	4.45
Relative light output	100	12	25	75	118
Decay time (ns)	230	300	60	40	40–70
Emission peak wavelength (nm)	410	480	430	420	420
Rugged	No	Yes	No	Yes	Yes
Hygroscopic	Yes	No	No	No	No

U.S. Pat. No. 4,958,080 to C. L. Melcher entitled "Lutetium Orthosilicate Single Crystal Scintillator Detector," which issued on Sep. 18, 1990, describes Ce:LSO.

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U.S. Pat. No. 5,025,151 to C. L. Melcher entitled "Lutetium Orthosilicate Single Crystal Scintillator Detector", which issued on Jun. 18, 1991, describes an apparatus that uses the Ce:LSO scintillator of the '080 patent to investigate subsurface earth formations.

"Czochralski Growth of Rare Earth Oxyorthosilicate Single Crystals" by C. L. Melcher et al. was published in J. Crys. Growth, vol. 128, p. 1001–1005, (1993) and describes using the Czochralski crystal growing method to prepare single crystals of Ce:GSO, Ce:LSO, and Ce:YSO.

U.S. Pat. No. 5,660,627 to R. A. Manente et al. entitled "Method of Growing Lutetium Oxyorthosilicate Crystals," which issued on Aug. 26, 1997, describes an improved Czochralski crystal growth method for growing an LSO crystal that displays substantially uniform scintillation behavior throughout the crystal. Also described is a scintillation detector used with the crystal. "Physical Processes in Inorganic Scintillators" by P. A. Rodnyi, p. 50, CRC Press, New York, N.Y. (1997), includes data relating to Ce:YSO.

Ideally, a crystal scintillator is inexpensive to produce, has a fast decay time, and is dense, bright, and is a rugged crystal. As The Table clearly demonstrates, the decision to use a particular scintillator involves compromises between the various physical properties. Although NaI(Tl) is a very bright crystal scintillator, it is not dense so that much of the radiation incident on the crystal is not absorbed by the crystal. Due to its hygroscopic nature, NaI(Tl) must be protected from moisture and because it is not rugged, it should not be used in applications where it is subject to fracture. Finally, NaI(Tl) has the relatively long luminescence decay time of over 400 ns.

BGO is almost twice as dense as NaI(Tl) and is a rugged and non-hydroscopic crystal. However, BGO is not as bright a crystal as NaI(Tl) and has an even longer decay time. Ce:GSO is also a dense crystal scintillator and is a brighter crystal than BGO. However, Ce:GSO is not a rugged crystal.

Ce:YSO is a bright, rugged, non-hygroscopic crystal. Importantly, the starting yttrium oxide Y_2O_3 which is used to grow Ce:YSO is relatively inexpensive, about $20/kg for 99.99% pure Y_2O_3. Ce:YSO has a melting temperature of about 2000° C., which is about 150 degrees lower than the melting temperature for Ce:LSO, making fabrication of Ce:YSO easier and less energy demanding than that for Ce:LSO. Unfortunately, Ce:YSO is not a very dense crystal, and decay times as long as 70 ns have been reported for this material.

Of the scintillators listed in The Table, Ce:LSO has the most desirable physical properties; it is a bright, dense, rugged, non-hygroscopic scintillator, and has a short decay time. However, Ce:LSO is extremely expensive, about $2,000/kg for 99.99% pure material. In addition, the processing temperature for growing Ce:LSO is very high; Lu_2O_3 and LSO melt at temperatures of about 2310° C. and 2150° C., which adds to the difficulty of growing crystals of growing Ce:LSO.

Efforts to provide oxyorthosilicate scintillators with a broader range of properties have led to the production of cerium-activated single crystal scintillators having compositions that include a variety of lanthanide elements in combination with Gd, Lu, and Y. Examples of these are described in the papers and patents that follow. "Czochralski Growth of Rare-Earth Orthosilicates (Ln₂SiO₅)" by C. D. Brandle was published in J. Crys. Growth, vol 79, p. 308–315, (1986) and provides an evaluation of the Czochralski method for growing GSO, YSO, and a variety of orthosilicates containing either Gd or Y doped with a lan-

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thanide series element. The reported combinations with Y were YSO doped with Ce, Pr, Nd, Sm, Gd, Tb, Er, Tm, and Yb. The reported combinations with Gd were GSO doped with Ce and Tb. "Czochralski Growth and Characterization of $(Lu_{1-x}Gd_x)_2SiO_5$" by G. B. Loutts et al. entitled was published in J. Crys. Growth, vol. 174, p. 331–336, (1997), and describes single crystal oxyorthosilicate scintillators having both Lu and Gd.

U.S. Pat. No. 4,647,781 to K. Takagi et al. entitled "Gamma Ray Detector," which issued on Mar. 3, 1987, describes a cerium-activated oxyorthosilicate scintillator having both Gd and Y and/or La. These scintillators have the general formula $Gd_{2(1-x-y)}Ln_{2x}Ce_{2y}SiO_5$ where Ln is yttrium and/or lanthanum, where $0 \leq x \leq 0.5$, and $1 \times 10^{-3} \leq y \leq 0.1$.

U.S. Pat. No. 5,264,154 to S. Akiyama et al. entitled "Single Crystal Scintillator," which issued on Nov. 23, 1993, describes a single crystal scintillator and apparatus for prospecting underground strata using the scintillator. The single crystal scintillator is a cerium-doped oxyorthosilicate having the general formula $Gd_{2-(x+y)}Ln_xCe_ySiO_5$ wherein Ln is Sc, Tb, Lu, Dy, Ho, Er, Tm, or Yb, $0.03 \leq x \leq 1.9$, and $0.001 \leq y \leq 0.2$.

Clearly, it is desirable to provide an affordable crystal scintillator having the most desirable properties for a particular application.

Therefore, an object of this invention is to provide an oxyorthosilicate crystal scintillator that can be used to detect gamma rays, x-rays, and the like.

Another object of the invention is to provide a crystal scintillator having excellent physical properties at a reasonable cost. Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

To achieve the foregoing and other objects, and in accordance with the purposes of the present invention as embodied and broadly described herein, the invention includes a transparent single crystal scintillator of cerium-activated lutetium yttrium oxyorthosilicate having the general formula $Lu_{(2-x-z)}Y_xCe_zSiO_5$, wherein $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$.

DETAILED DESCRIPTION OF THE INVENTION

The present invention includes a single crystal scintillator containing lutetium and yttrium and having the general formula $Lu_{(2-x-z)}Y_xCe_zSiO_5$ where $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$. The invention also includes a scintillation detector for detecting gamma rays, x-rays, and the like using the crystal scintillator. The crystal scintillators of the present invention were grown using two conventional crystal growing processes: (1) the "Optical Float zone" method, and (2) the "Czochralski" method. The starting oxide materials used were Lu_2O_3, CeO_2, Y_2O_3, and SiO_2, and each had a purity of 99.99%.

A crystal of the present invention was grown by the optical float zone method by first blending Lu_2O_3 (71.4487 g), CeO_2 (0.1721 g), Y_2O_3 (4.5049 g), and SiO_2 (12.0169 g) in a mixer/mill for 30 minutes to give the composition

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$Lu_{1.7933}Y_{0.1995}Ce_{0.0050}SiO_{5.0025}$. The blended powder was loaded into a latex cold isostatic pressing (CIP) tube and pressed to about 7000 N/cm^2 for about 5 minutes. The resulting pressed rods were fired at about 1100° C. for about 8 hours to impart additional mechanical stability. After cooling, the rods were mounted in a dual halogen optical float-zone crystal growth furnace using platinum wire for fixturing. A single crystal was grown at a rate of about 2.0–2.5 mm/hr under flowing air using a seed crystal of Ce:LSO and standard float zone procedures. A stable molten zone was established between the seed crystal and the feed rod, which were counter-rotated at 45–60 rpm and passed through the hot zone.

The measured light output of the above single crystal of the present invention indicated that the crystal was as bright as Ce:LSO crystals made by the same crystal growing process. The measured crystal density of 7.1 g/cm^3, which is identical to the density calculated by rule of mixtures, was only slightly lower than the reported density of 7.4 g/cm^3 for Ce:LSO. The measured peak emission wavelength for the single crystal of the present invention was 420 nm.

A larger crystal having the same powder blend composition as the first was grown using the Czochralski method, which is discussed in the 1986 paper to D. C. Brandle et. al. as previously described. About 320 g of starting oxide powder was blended and charged into an iridium crucible. Under a nitrogen atmosphere and using an iridium seed rotated at about 30 rpm, a 15-mm diameter single crystal was grown at a crystal growth rate of 1.5 mm/hr. The crystal was dense, bright, non-hygroscopic and rugged. The measured luminescence decay for this crystal was about 35–45 ns. For comparison, a crystal of Ce:LSO were grown by the Czochralski method. Less power was required to grow the crystal of the present invention than to grow the Ce:LSO crystal.

The optical float zone method was also used to grow additional crystals of the present invention, which included crystals from the starting blended oxide powders $Lu_{1.1970}Y_{0.7980}Ce_{0.0050}SiO_{5.0025}$ and $Lu_{0.9975}Y_{0.9975}Ce_{0.0050}SiO_{5.0025}$.

The crystal scintillators of the present invention can be used in a scintillation detector. To provide the scintillation detector, the crystal scintillator is optically coupled to a photodetector, which produces an electrical signal in response to light produced from the crystal scintillator in response to gamma rays, x-rays, and the like radiation incident upon the crystal scintillator. A wide variety of photodetectors can be used, such as photomultiplier tubes, photodiodes, microchannel plates, charge-coupled devices such as video cameras, etc. The crystal can be coupled to the photodetector by any of a variety of well-known coupling mechanisms or devices such as optical fibers, lenses, mirrors, grease, etc.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

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What is claimed is:

1. A crystal scintillator comprising a transparent single crystal of cerium-activated lutetium yttrium oxyorthosilicate having the general formula $Lu_{(2-x-z)}Y_xCe_zSiO_5$, wherein $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$.

2. The crystal scintillator of claim 1, wherein $0.2 \leq x \leq 1.8$.

3. The crystal scintillator of claim 2, wherein said scintillator has a luminescence wavelength of about 420 nm.

4. The crystal scintillator of claim 3, wherein said scintillator has a luminescence decay time of about 35–45 ns.

5. A scintillation detector, comprising:

(a) a crystal scintillator comprising a transparent single crystal of cerium-activated lutetium yttrium oxyorthosilicate having the general formula $Lu_{(2-x-z)}Y_xCe_zSiO_5$, wherein $0.05 \leq x \leq 1.95$ and $0.001 \leq z \leq 0.02$; and

(b) a photodetector optically coupled to said crystal scintillator for detecting light from said crystal scintillator.

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6. The detector of claim 5, wherein said photodetector comprises a photomultiplier tube.

7. The detector of claim 5, wherein said photodetector comprises a charge-coupled device.

8. A scintillation detector, comprising:

(a) a crystal scintillator comprising a transparent single crystal of cerium-activated lutetium yttrium oxyorthosilicate having the general formula $Lu_{(2-x-z)}Y_xCe_zSiO_5$, wherein $0.2 \leq x \leq 1.8$ and $0.001 \leq z \leq 0.02$; and

(b) a photodetector optically coupled to said crystal scintillator for detecting light from said crystal scintillator.

9. The detector of claim 8, wherein said photodetector comprises a photomultiplier tube.

10. The detector of claim 8, wherein said photodetector comprises a charge-coupled device.

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Adverse Decision In Interference

Patent No. 6,323,489, Kenneth J. McClellan, SINGLE CRYSTAL SCINTILLATOR, Interference No. 105,083, final judgment adverse to the patentee rendered April 28, 2003, as to claims 1-10.
(Official Gazette June 10, 2003)